NEW APPLICATIONS OF EQUATIONS OF STATE IN MOLECULAR MOD-

ELS OF COMPLEX FLUID MIXTURES

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ABSTRACT

Two different types of problems are approached by connecting simplified molecu-

lar models with EOS. For aqueous-organic solutions of gases chemically reacting with

solvent special technique to handle electrostatic and nonelectrostatic interaction contribu-

tions in the calculation of liquid composition and fugacity coefficients is applied for mod-

eling VLE. Modified hole model and SRK EOS are utilized to describe solubility of gases

in water - alkanolamine -acid gas (CO, H,S) mixtures. A polydisperse version of thermo-

dynamic micellization model proposed earlier is formulated and applied to describe

asphaltene phase drop-out from crude oils.

INTRODUCTION

Many advanced versions of EOS were proposed for molecular fluids in the recent

decade. While these allowed reliable description of phase behavior for a great number of

important molecular fluid systems, the interest in phase equilibria modeling shifts to more

and more complex fields, such as chemically reacting systems, electrolyte and polymer

systems over a wide range of temperature and pressure, micellar solutions, microemulsions,

etc. The present work is focused on phase equilibria modeling for two types of complex

fluids: aqueous organic systems containing chemically reacting gases, and fluid systems,

in which agglomeration into large aggregates (micelles) takes place, owing to the pres-

ence of amphiphilic moieties in the solution.

AQUEOUS ALKANOLAMINE SOLUTIONS OF ACID GASES

Phase equilibria modeling in chemically reacting fluid mixtures is important for many practical tasks, chemical absorption of gases in aqueous solutions is among them [1]. In particular, aqueous alkanolamine solutions are widely used for removal of acid gases (hydrogen sulfide, carbon dioxide) from refinery gas streams. These processes are classified as chemical absorption because the acid gases react with the alkanolamine forming nonvolatile ionic species.

The following chemical reactions occur in aqueous alkanolamine solutions of CO and H_.S:

$$CO_{2} + H_{2}O \Leftrightarrow HCO_{3}^{-1} + H^{+} \qquad HCO_{3}^{-1} \Leftrightarrow CO_{3}^{-2} + H^{+} \qquad (1)$$

$$H_{2}O \Leftrightarrow H^{+} + OH^{-} \qquad RR'R''N + H^{+} \Leftrightarrow RR'R''NH^{+}$$

$$H_{2}S \Leftrightarrow HS^{-} + H^{+} \qquad HS^{-} \Leftrightarrow S^{2-} + H^{+}$$

In these equations RR'R'N represents alkanolamine, where at least one of R, R' and R'' is alkoxy group, others are alkyl group or hydrogen. Primary and secondary amines may also react directly with CO₂ to form stable carbamates:

$$RR'NH + CO_2 \iff RR'NCOO' + H^+.$$

Due to the chemical reactions the liquid phase contains both molecular and ionic species. Only molecular species are volatile, so the conditions of vapor-liquid equilibrium reduce to the equalities of chemical potentials of CO_2 (or H_2S), H_2O , RR'R''N in the coexisting phases. The condition of chemical equilibrium yields the following equation for chemical reaction R:

$$K_R(T) = \prod_i a_i^{\mathsf{V}_{i,R}} \tag{2}$$

where K_R is the equilibrium constant for reaction R, a_i is the activity of component i, and $V_{i,R}$ is the stoichiometric coefficient of component i in reaction R. The "true composition" of the liquid phase for a given temperature and overall composition can be found from Eqs. (2), the mass balance equations, and the condition for liquid phase electroneutrality, if the activity coefficients of the species in their dependency on the "true concentration" are known.

The methods of calculating the solubility of acid gases in aqueous amine systems used until now (short reviews can be found in [2,3]) are based on an activity coefficient model for the liquid phase and a separate model for the vapor phase. Successful correlation of the VLE data was obtained using the Pitzer model for the liquid solution and virial EOS for vapor [4]. An alternative way of modeling high-pressure phase equilibria is the use of a single equation of state describing both the vapor and liquid phases. For nonelectrolyte systems this way of modeling phase equilibria is well developed and is applied very successfully. However until recently this approach was not tested for the systems under study. The first attempt was reported in [3] where a special modification of a hole model was considered. In the present communication the proposed approach is applied to CO₂ - N-methyldiethanolamine (MDEA) - H₂O and H₂S - MDEA - H₂O systems with the use of modifications of the hole model (HM) and the Soave-Redlich-Kwong (SRK) EOS.

VLE Modeling

The original versions of HM [5] and SRK EOS [6] can be applied without any changes to the vapor but not to the liquid solution, which contains both molecular and ionic species. The models were modified in such a manner that the "true composition" of liquid solutions and electrostatic interactions could be taken into account. For the activity coefficient γ_i^l of species i in the liquid solution we write:

$$\ln \gamma_i^l = \ln \gamma_{nonel,i}^l + \ln \gamma_{el,i}^l, \tag{3}$$

where is the electrostatic contribution $\ln \gamma_{el,i}^l$ and $\ln \gamma_{nonel,i}^l$ is the nonelectrostatic part derived from the EOS in the same way as for molecular fluids. The Debye-Huckel approximation modified by Pitzer [7] was used to represent $\gamma_{el,i}^l$. Taking into account Eq.(3) and relationship between fugacity coefficient φ_i^l and activity coefficient we obtain:

$$\ln \varphi_i^l = \ln \varphi_{nonel,i}^l + \ln \gamma_{el,i}^l,$$
 where $\varphi_{nonel,i}^l$ relates to EOS as usually. (4)

Thus, expressions for activity and fugacity coefficients of molecular and ionic species in liquid solution were obtained, but it would be impractical to consider a detailed

model of interactions between the species and to introduce a great number of adjustable parameters. The proposed simplifications are as follows.

It is assumed that $\gamma_{nonel,i}^l$ ($\varphi_{nonel,i}^l$) for molecular forms of CO₂, HS, HO and RR'R'N can be estimated from EOS with regard only to the overall composition of the liquid phase that is in the same manner as for the system without chemical reactions. The next approximation (in conformity with the preceding one) concerns calculations of the "true composition" from Eqs. (2), a procedure where the knowledge of factor $\prod_i \gamma_i^{v_i}$ for every reactions (1) is needed. An assumption is made that the concentration dependency of this factor is governed only by electrostatic activity coefficients γ_{eli}^l .

In the case of SRK EOS the following conditions of VLE are used:

$$(x_i \varphi_i)^{(v)} = (x_i \varphi_i)^{(l)}, \qquad i = CO_2(H_2S), H_2O, RR'R'N$$
 (5)

where x_i is the true mole fraction and φ_i is the fugacity coefficient of component i.

Calculations can be performed as follows. The temperature and the overall masses of the components in the liquid phase are fixed, the composition of the vapor phase is varied to find the values satisfying Eqs. (5). For given overall concentrations of carbon dioxide (or hydrogen sulfide) and RR \H N Eqs. (2), material balance equations, and condition of electroneutrality are used to calculate the true concentration (x_i^l) of each species i in the liquid phase. Following the arguments given above only the Debye-Huckel contribution to the activities is considered in this step. In the next step the fugacity coefficients $\varphi_{nonel.i}^l$ for neutral species are calculated from SRK with regard to overall composition of the mixture (the electrostatic contribution is included for water).

A composition dependent non-quadratic mixing rule is used for the attraction parameter of SRK EOS [8]. Two temperature dependent interaction parameters are involved for each binary subsystem.

For the hole model conditions of vapor-liquid equilibrium are formulated as follows:

$$(\widetilde{x}_i\widetilde{\gamma}_i)^{(v)} = (\widetilde{x}_i\widetilde{\gamma}_i)^{(l)}, \qquad i = CO_2(H_2S), H_2O, RR'R'N \text{ and holes.}$$
 (6)

Here $\tilde{\chi}_i^{\nu}$ and $\tilde{\chi}_i^{l}$ are mole fractions of species i in the vapor and liquid mixtures of molecular species, ions (present in the liquid phase), and holes; $\tilde{\gamma}_i^{\nu}$ and $\tilde{\gamma}_i^{l}$ are activity coefficients. Eq.(6) for holes represents the condition of mechanical equilibrium. The computational procedure was outlined earlier [3].

The models were applied to aqueous solutions of N-methyldiethanolamine (MDEA). HM model parameters for pure components $\frac{H}{2}O$, $\frac{CO}{2}$ and $\frac{H}{2}S$ were taken from [9]. Each of the binary systems was characterized with a single energetic parameter, the quantity being temperature dependent. The HM parameters of $\frac{CO}{2}$ - $\frac{H}{2}O$ and $\frac{H}{2}S$ - $\frac{H}{2}O$ interactions were estimated using vapor-liquid equilibrium data for diluted aqueous solutions of $\frac{CO}{2}$ and $\frac{H}{2}S$ in the temperature range from 293 to 453 K, as it was described in [3]. The Soave correlation was utilized to find SRK parameters for pure supercritical components $\frac{CO}{2}$, $\frac{H}{2}S$). SRK parameters for $\frac{H}{2}O$ and MDEA were estimated from experimental data on saturated vapor pressure and liquid density of the pure component in subcritical region. For evaluating binary SRK parameters the same experimental VLE data for $\frac{CO}{2}$ - $\frac{H}{2}O$ and $\frac{H}{2}S$ - $\frac{H}{2}O$ systems were used as in the case of HM.

As no experimental data on the vapor-liquid equilibrium for the CO₂ - MDEA and H₂S - MDEA binaries are available, ternary data have to be used to estimate parameters of interaction between these two components. The use of ternary data in this case is explained also by the aforementioned argument: the model for the ternary systems deals with some effective CO₂-MDEA or H₂S-MDEA parameters averaged over molecular and ionic species in the range of concentrations studied here. The general procedure of calculation for ternary systems for both models was similar, and it was described in [3]. Knowledge of the temperature dependent equilibrium constants for chemical reactions (1) is required for the calculations. These constants were taken from the literature [4].

In calculations by HM one temperature dependent parameter relating to CO₂-MDEA interactions in the CO₂-MDEA-H₂O system (or to the H₂S-MDEA interactions in the H₂S-MDEA-H₂O system) was adjusted using ternary vapor-

liquid equilibrium data (in total three parameters were involved). Two temperature dependent SRK parameters (in total four parameters) were determined from the ternary data. The results of modeling are presented in Figs.1, 2. The both models permit to describe roughly the influence of the CO₂ (or H_S) and MDEA concentrations on the vapor pressure of the ternary solutions at 313-413 K but the average deviations of the calculated results from the experimental data [4] exceed the experimental error, especially for 313 K. The model performance is better for the system containing CO₂, than for the system with H_S.

THERMODYNAMIC MODEL OF ASPHALTENE AGGREGATION AND DEPOSITION

Asphaltenes are contained in heavy polyaromatic fractions of crudes [11,12] and under certain conditions drop out causing bad problems in oil production. Prediction of the onset of precipitation and the amount of the asphaltene phase is an important problem unsolved so far. The complexity of this problem is aggravated by the fact that it is extremely difficult (if possible) to specify unambiguously asphaltenes as definite molecular entities: asphaltene is a general name encompassing a great diversity of molecular species. According to the so-called operational definitions, which are of major use in practice, asphaltenes are substances that precipitate from a crude upon titration by pentane [13]. In the crudes polar asphaltene materials associate and form large aggregates (micelles) with bipolar resins [12,14]. Stable dispersions of aggregated particles are present prior to asphaltene deposition.

Although aggregation and colloid nature of asphaltene-containing crudes is a well-established experimental fact, until recently the attempts to model these systems were mainly focused on the application of bulk-solution models to describe asphaltene solubility [13,15], and it is not surprising that these attempts were not very encouraging. The only thermodynamic colloid models proposed for apshaltenes are those by Leontaritis and

Mansoori (LM) [16], and Victorov and Firoozabadi (VF) [10], which latter was substantially revised recently [17] by introducing the assumption of spherical aggregates and applying pseudophase approximation. The VF model incorporates a bulk-phase EOS into the aggregation model, which enables the consideration of pressure effects. Although the LM, unlike VF, does not consider details of the structure of aggregated solution (aggregation numbers, size-distribution, micellar structure and shape), both models bear much more similarities, than it might appear at first sight (e.g., role of the resins adhering to asphaltene surface, formulation of both models in terms of coverage fraction, assumption of pure asphaltene precipitate implying the constancy of its chemical potential, when a precipitant is added to the crude at constant pressure and temperature in liquid titration). The VF model allows consideration of aggregate-size distribution, though only its monodisperse version was tested [10]. The distribution over aggregation numbers was studied in [17], where several important new factors were incorporated into the model, and promising results were obtained. However, the consideration of spherical asphaltene aggregates [17] instead of plate-like ones, which of course somewhat simplifies the treatment, is not in line with most experimental observations [18], and general notion that large and polydispersed aggregates, which is the case for asphaltenes [20], are not spherical [19]. In the present paper we return to the original formulation of the VF model assuming platelike aggregates, but consider the distribution of aggregates over their sizes.

The VF utilizes the ideas of micellar systems thermodynamics [19], whose major target was, traditionally, aqueous surfactant solutions. The aggregation equilibrium between monomeric species and a micelle containing \mathbf{n}_1 asphaltene and resin monomers \mathbf{n}_2 is expressed as [10,19]:

$$\mu_{M}^{\beta} = n_{1} \mu_{M}^{\beta} + n_{2} \mu_{T}^{\beta}. \tag{9}$$

where $\mu_{_M}^{_\beta}$, $\mu_{_{a1}}^{^\beta}$, and $\mu_{_{r1}}^{^\beta}$ are chemical potentials of a micelle and the monomers, respectively. For a diluted solution we have:

$$X_{M} = X_{a_{1}}^{n_{1}} X_{r_{1}}^{n_{2}} \exp\{\Delta G_{M}^{00} / kT\},$$
(10)

where X_i is the mole fraction of species i, and ΔG_M^{00} is the standard Gibbs energy of micellization. Given that the aggregation numbers are large, Eq.(10) may hold even up to some substantial gross concentrations of resins and asphaltenes; many oils, except heavy bitumen, are likely to conform to this approximation. For diluted solutions the aggregation process is entirely determined by the standard Gibbs energy of micellization, in which three major contributions are discerned [10], as follows. 1) The main driving force of aggregation is the solvophobic effect, which impels the monomeric asphaltenes into micelles. When micelles are destroyed, asphaltenes are expelled from crude (due to their low bulk solubility) to form the asphaltene precipitate. Solvophobic term is expressed via X_{a1}^{ons} , the fraction of monomeric asphaltenes in petroleum fluid at equilibrium with the bulk phase of pure asphaltenes. This principal parameter of the theory reflects the individuality of a crude (and its asphaltenes) and should be determined from experimental data (in principle a single experimental point may be sufficient). Once estimated, this parameter determines the behavior of a given crude with respect to asphaltene drop-out (various titrants added, pressure influence, etc.). 2) A contribution owing to the transfer of resin molecules from the bulk of crude into a micelle. It consists of a constant energy-term, ΔU_r , and an entropic term, which depends upon the occupation fraction, $\theta = A_r (n_2) / A_{\Sigma}$. Here A_{Σ} is the total surface area of the aggregate, and $A_{r}\left(n_{2}\right)$ is the surface area of the asphaltene micellar core covered by resins. 3) A contribution related to the interfacial tension σ_0

of the asphaltene core/petroleum interface and its decrease owing to the adsorption of amphiphile resin molecules. This term accounts for the geometry of aggregates. Plate-like aggregates are considered, in accordance with spectroscopic evidence [18], and for simplicity the cores are treated as coin-shaped. Resin molecule polar heads are supposed to accommodate only on the flat surfaces of the aggregate. Thence:

$$\theta = n_2 a / \left(2n_1 \mathbf{v_a} / r + 2\pi r^2 \right) \tag{11}$$

where v_a is the volume per asphaltene monomer, a is the effective surface area of the

adsorbed resin molecule head, r is the micelle core radius.

The EOS is used to account for the dependence of solvophobic term on the state variables of aggregated fluid. The change in equilibrium concentration \mathbf{X}_{a1}^{ons} is governed by the fugacity of the bulk asphaltene phase, which is equal to the fugacity of monomeric asphaltenes in the crude. This latter can be calculated using a bulk-fluid EOS, the association and aggregation do not matter anymore in the first approximation, since the solution is diluted with respect to monomeric asphaltenes. Provided a value of \mathbf{X}_{a1}^{ons} at some conditions (\mathbf{X}_{a10}^{ons}) is known, the dependence of \mathbf{X}_{a1}^{ons} on state variables is fully determined by the EOS.

With the model described above Eq.(10) takes the form:

$$X_{M}(n_{1}, n_{2}) = \psi_{a}^{n_{1}} \psi_{r}^{n_{2}}$$
where $\psi_{a} = X_{a1} / X_{a1}^{ons}$, $\psi_{r} = X_{r1} \exp f(\Theta)$, and
$$f(\Theta) = \ln(1 - \Theta) + \frac{\Delta U_{r}}{RT} - \frac{\sigma_{0} a(1 - \Theta)}{RT\Theta}$$
(12)

Polydispersity of aggregated asphaltene particles

The distribution of aggregates over their size should be accounted for in the material balance equations, which relate concentrations of micelles and monomers to the gross-concentrations (X_a, X_r) of asphaltenes and resins in the crude:

$$X_{a} = X_{a1} + \sum_{n_{1}, n_{2}}^{\infty} n_{1} X_{M}(n_{1}, n_{2}), X_{r} = X_{r1} + \sum_{n_{1}, n_{2}}^{\infty} n_{2} X_{M}(n_{1}, n_{2})$$
(13)

where the summation extends over all $\mathbf{n_1}$ and $\mathbf{n_2}$ values, and should start from some minimal $\mathbf{n_{10}}$ and $\mathbf{n_{20}}$ corresponding to the smallest possible aggregate. If no additional assumptions are made, one has to decide, which particular aggregate shape is stable for a given pair of $\mathbf{n_1}$, $\mathbf{n_2}$ and calculate $X_M(n_1,n_2)$ from Eq.(10) applying the ΔG_M^{00} -model for this aggregate shape. The most probable aggregate composition is found from the condition $(\partial \ln X_M/\partial \mathbf{n_2})_{\mathbf{n_1}} = 0$ [19], which gives in the case of plate-like aggre-

gates

$$\ln(1-\Theta) - \frac{\Theta}{(1-\Theta)} = -\ln X_{r1} - \frac{\Delta U_r}{RT} - \frac{\sigma_0 a}{RT}$$
(14)

The solution of this equation $\Theta = \Theta^*$ is the optimum coverage fraction. Note that Θ^* depends neither on the micellar size, nor on the shape, but is completely determined by X_{r1} and the model parameters a, ΔU_r , and σ_0 . At fixed Θ there is only explicit dependence of X_M upon \mathbf{n}_1 and \mathbf{n}_2 given by Eq. (12), though it is necessary to ensure the consistency of \mathbf{n}_1 , \mathbf{n}_2 , and Θ^* values, when performing summations in Eq.(13). Minimal $\mathbf{n}_2 = \mathbf{n}_{20}$ at given \mathbf{n}_1 and Θ^* corresponds to a cylindric core with flat surfaces fully covered with resins (smallest possible cylinder radius). This leads to $\mathbf{n}_{20} = k\mathbf{n}_1^{2/3}$, where

$$k = \frac{2\pi}{a} \left(\frac{\mathbf{v_a}}{\pi} \frac{\boldsymbol{\Theta}^*}{1 - \boldsymbol{\Theta}^*} \right)^{2/3}$$
. The summation over all $\mathbf{n_2}$ will roughly correspond to

the summation over all possible radii and thicknesses consistent with the given $\boldsymbol{\Theta}^*$.

The calculation of the number average aggregation numbers [19] requires the

estimation of the sums
$$S_1 = \sum_{n_1 = n_{10}}^{\infty} n_1 \psi_a^{n_1} \sum_{n_2 \ge k n_1^{2/3}}^{\infty} \psi_r^{n_2}$$
,

$$S_2 = \sum_{n_1 = n_{10}}^{\infty} \psi_a^{n_1} \sum_{n_2 \ge kn_1^{2/3}}^{\infty} n_2 \psi_r^{n_2}, \text{ and } S_0 = \sum_{n_1 = n_{10}}^{\infty} \psi_a^{n_1} \sum_{n_2 \ge kn_1^{2/3}}^{\infty} \psi_r^{n_2}, \text{ in}$$

which summations over \mathbf{n}_2 are carried out analytically, while those over \mathbf{n}_1 are performed numerically. Using this procedure of summation we solved Eqs. (13,14) iteratively for monomer concentrations $(\mathbf{X}_{a1},\,\mathbf{X}_{r1})$ and $\boldsymbol{\Theta}^*$. Having obtained the average aggregation numbers, one can estimate the mean radius of the aggregate population from Eq. (11).

The above procedure has been applied to model titration of asphaltenes from a tank oil by liquid n-alkanes [13]. The composition of the tank oil was modeled in the same way as before [10], and the Peng-Robinson EOS with the same parameter values was used for

monomer fugacity calculations. The micellization parameters retained the values used with the monodispersed version of the model [10], viz.: X_{a10}^{ons} = 2.4 10^{-3} , ΔU_r = 0.073 J/ (mol m²), σ_0 = 0.040 N/m, and a = 40 Ų. In addition to these the lowest number of asphaltene monomers in a plate-like aggregate, \mathbf{n}_{10} , has to be specified in the calculations. Since spherical aggregates are normally observed at aggregation numbers of about 30-100 [19], we chose \mathbf{n}_{10} = 40.

The distribution of micelles over aggregation numbers (12) is a rapidly decaying function (as it is the case for large prolate cylindric aggregates [19]). This suggests probable coexistence of plate-like aggregates with spherical ones [16].

The modeling of titration with n-alkanes shows almost the same results as obtained before [10], given that average asphaltene aggregation numbers in both monodisperse and polydisperse versions are close (Fig.3). As it might be expected, the total amount of precipitate is slightly less in the polydisperse case, in which more asphaltene material remains aggregated in the crude. The onset of precipitation shifts to somewhat lower dilution ratios (0.6, cf. 1.0 for the monodisperse case), owing to the presence of both more and less stable aggregates in the solution.

The average aggregation numbers are shown in Fig.4. While the asphaltene average aggregation number remains almost constant with dilution, the resin average aggregation number first decreases (as the resins are washed away from micellar coronas by a titrant) and then remains roughly constant starting from the onset of precipitation. The aggregation number rapidly decreases at critical micelle concentration. Similar results are found for the titration with other alkanes of medium chain length. As in the monodisperse case, addition of longer-chain n-alkanes does not cause precipitation.

CONCLUSION

The models discussed above relate to two fields of new applications of EOS and present some development of recently proposed methods [3,10].

The results of modeling of solubility of CO₂ and H₂S in aqueous alkanolamine systems confirm that the approach proposed in [3] is promising in the search for the predictive models of both vapor and liquid phases in aqueous-organic systems with chemically reacting solutes. The present work has shown that the approach formulated firstly in application to HM can be used with other EOS. There are several ways improve the model descriptive abilities, and it would be of special interest to try more sophisticated approximations for the electrostatic contribution to activity coefficients.

A polydisperse version of the VF thermodynamic micellization model of asphaltene systems [10] is formulated and compared with the original monodisperse version. The results obtained with the aid of both models are very similar, however one parameter less is required for calculations by the polydisperse model. Calculated results suggest that consideration of polymorphic aggregates is likely to advance the model. Further work in this direction is worth to be continued. The application of the approach is not limited to asphaltene systems. Its use for describing other diluted solutions with aggregation seems promising.

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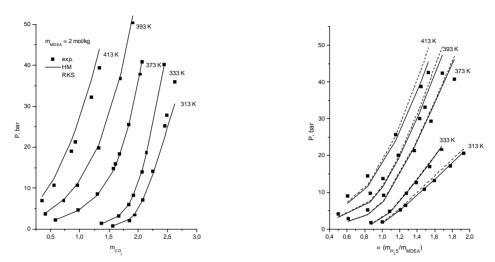


Fig. 1. Solubility of carbon dioxide in aqueous solutions of MDEA: experimental data at $m_{MDEA} = 2 \text{ mol/kg}$ [4] (points), results from SRK (solid lines) and HM (dashed lines). Fig. 2. Solubility of hydrogen sulfide in aqueous solutions of MDEA: experimental data at $m_{MDEA} = 2 \text{ mol/kg}$ [4] (points), results from SRK (solid lines) and HM (dashed lines).

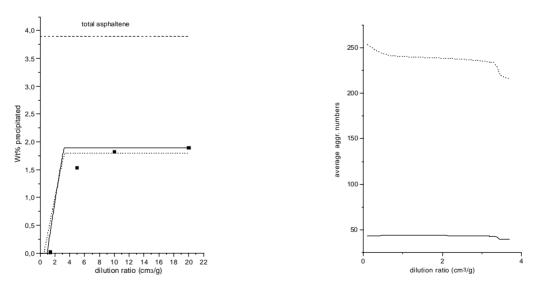


Fig 3. Liquid titration curves for tank oil with n-heptane (295 K) calculated by VF monodisperse [10] (solid line) and polydisperse version (dotted line) of the model. Points are the experimental data [13].

Fig 4. Average aggregation numbers for asphaltenes (solid line) and resins (dotted line) for titration of tank oil [13] with liquid n-heptane at 295 K.

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